

UNITED STATES  
ATOMIC ENERGY COMMISSION

OAK RIDGE OPERATIONS  
P.O. BOX E  
OAK RIDGE, TENNESSEE 37830

CR

AREA CODE 615  
TELEPHONE 483-6611

July 22, 1970

Cys fwd by FRB to:

F.L.Culler (3)  
J.H.Gibbons  
J.L.Liverman  
A.H.Snell  
J.C.White  
M.E.Ramsey (3)

7/24/70

*N. E. Bolton*  
*T. A. Lincoln*  
*W. H. Jordan - de info.*

Mr. S. Leary Jones  
Director, State of Tennessee's  
Water Pollution Control Board  
Public Health Department  
344 Cordell Hull Building  
Nashville, Tennessee

MERCURY SAMPLING IN OAK RIDGE AREA

Dear Mr. Jones

Reference is made to the letter from F. L. Culler of our ORNL to you dated July 9, 1970, discussing mercury sampling in the Oak Ridge area.

We actually have had a limited mercury sampling program in the Oak Ridge area for about six years as noted in the enclosed report prepared by N. E. Bolton of our ORNL. We expanded our program to collect additional data when information regarding the fish problems in the Great Lakes first came to our attention. The enclosed report shows mercury concentrations for several years in effluent leaving our ORNL area as well as those upstream and downstream in the Clinch River. Included also are results of our more extensive recent sampling program and some data on coliform counts in the Clinch River. The report tends to indicate that current Hg concentrations in the Clinch River range less than 5 ppb near and below Oak Ridge. Unfortunately, we do not have any mercury analyses on fish from the Clinch River, but are requesting our ORNL to undertake a modest one-time sampling to provide some data in this regard.

While not included in the attached report, our liquid effluent from New Hope Settling Basin at Y-12 also ranges below 5 ppm soluble mercury. We recently sampled a few fish living in the New Hope Basin and near the effluent discharge point which becomes the east fork of Poplar Creek. The mercury concentration in these fish ranged around 0.7 ppm by our technique which is still under study. One of these samples is noted in the attached report. Fish purchased in a local store, which we sampled to check our technique, ranged up to 0.7 ppm mercury also. Of course, these store fish were not of local origin.

This document has been approved for release  
to the public by:

*Dan R. Hamm* 4/29/96  
Technical Information Officer Date  
ORNL Site

*F. L. Bruce*

COPY

S. Leary Jones

- 2 -

July 22, 1970

We would be pleased to discuss our sampling programs and results with you further and will provide additional meaningful data when it becomes available.

Sincerely,

*J. A. Lenhard*  
Joseph A. Lenhard, Director  
Safety Division  
Oak Ridge Operations

OS:JAL

Enclosure:  
N. E. Bolton's Report, 7/17/70

cc w/encl:  
A. G. Linton, FWQCA

cc w/o encl:  
R. C. Armstrong, AMO  
C. A. Keller, Prod. Div.  
H. M. Roth, LUD  
✓ F. R. Bruce, ORNL



UNITED STATES  
ATOMIC ENERGY COMMISSION

OAK RIDGE OPERATIONS  
P.O. BOX E  
OAK RIDGE, TENNESSEE 37830

AREA CODE 615  
TELEPHONE 483-8611

July 21, 1970

Distribution:  
J. L. Liverman

Union Carbide Corporation  
Nuclear Division  
Post Office Box X  
Oak Ridge, Tennessee

Attention: Dr. A. M. Weinberg, Director  
Oak Ridge National Laboratory

LIAISON WITH STATE AND FEDERAL AIR AND WATER POLLUTION CONTROL AGENCIES

Gentlemen:

Reference is made to the letter dated July 9, 1970, from F. L. Culler to S. Leary Jones of the State of Tennessee Water Pollution Control Board. This letter indicates an intention to commence mercury sampling locally and further suggests the possibility of sample analysis assistance to the State.

We are most interested in cooperating with State and Federal water pollution control agencies as we are certain you are. However, it will be necessary for formal contacts regarding pollution control matters related to AEC plants to remain with ORO as has been specified in OR Manual Chapter issuances. In particular, commitments for increasing our sampling or control programs or providing sampling results to outside groups should come from our OR office. This is deemed necessary since AEC facilities are responsible to satisfy the requirements of national air and water quality criteria and have been requested to deal with State and local groups and standards only through these Federal bodies.

With regard to mercury sampling, we were led to understand that your industrial hygiene group has been performing Hg sampling of ORNL effluents and that the results have been less than 10 ppb. If you wish to provide more elaborate or detailed sampling results, we will make these available, as appropriate, to interested groups.

ORIGINAL

Union Carbide Corporation

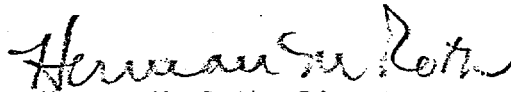
- 2 -

July 21, 1970

We will be happy to receive a specific proposal for providing sample analysis assistance to the State of Tennessee.

Your cooperation in this matter will be appreciated.

Sincerely,

A handwritten signature in cursive script, reading "Herman M. Roth".

Herman M. Roth, Director  
Laboratory and University Division  
Oak Ridge Operations

OS:JAL

cc: R. F. Hibbs, UCC-ND  
R. C. Armstrong  
J. A. Lenhard

# OAK RIDGE NATIONAL LABORATORY

OPERATED BY  
UNION CARBIDE CORPORATION  
NUCLEAR DIVISION



POST OFFICE BOX X  
OAK RIDGE, TENNESSEE 37830

cc: F. E. Bruce  
J. S. Gilberts  
J. L. Liverman  
R. H. Roth, CSE  
A. S. Snell  
J. C. White

CR

July 9, 1970

Mr. S. Leary Jones  
Director, State of Tennessee's  
Water Pollution Control Board  
Public Health Department  
344 Cordell Hull Building  
Nashville, Tennessee

Dear Mr. Jones:

When I talked with you and Floyd Larson in Nashville, we discussed methods of analysis for mercury in low concentrations. I asked Dr. J. C. White, of our Analytical Chemistry Division, to review our experience, and I am attaching a memorandum that he sent me. It appears that we do have capability for mercury analyses to levels of a few tenths parts per billion.

We have not analyzed routinely for mercury in water samples taken in local streams and lakes; however, we will start analyzing for mercury in samples that are taken locally. Mr. F. R. Bruce, our Associate Director for Administration, will have data available from time to time, which I am asking him to send to you. You may wish to discuss methods and analytical assistance directly with Jim White.

We will be glad to help in determining the mercury burden in Tennessee waters by making analytical techniques available and, assuming that satisfactory arrangements can be made, by running samples here.

Very truly yours,

A handwritten signature in cursive script that reads "Floyd L. Culler".

Floyd L. Culler  
Deputy Director

FLC:vmw  
Attachment

cc: Floyd L. Larson  
Water Resources Research Center  
The University of Tennessee

# INTRA-LABORATORY CORRESPONDENCE

OAK RIDGE NATIONAL LABORATORY

June 23, 1970

To: F. L. Culler


Subject: Determination of Mercury in Lake and River Waters

Here is some preliminary information on the topic of Hg in lake water. I have found that Y-12 has analyzed carp, taken from the Clinch River, for Hg and discovered 0.5 ppm in at least one sample. I think that is near or above the "tolerance level." Y-12 has also developed a very simple modified atomic absorption method that has a reported sensitivity of 0.2 parts per billion—really remarkable sensitivity. We plan to adopt this technique if it is at all as good as reported.

We have work underway on the activation analysis method (ORR) which will be as sensitive but much more complex than Y-12's method. I'll have results within a day or two on samples of water from Walker Branch and other locations in the area.

We also have an idea (Shults) for monitoring water for Hg using an electro-analytical (anodic stripping) technique that should be equally sensitive and relatively simple. One of our graduate students and a summer participant are working on this. If the initial results are promising, we intend to push this approach.

I'll keep you posted on these developments.



J. C. White  
Analytical Chemistry Division

JCW:bey

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\*Attachment to July 9, 1970 letter from F. L. Culler  
to S. Leary Jones, Tennessee Water Pollution Control Board

# INTRA-LABORATORY CORRESPONDENCE

OAK RIDGE NATIONAL LABORATORY

August 10, 1970

This document has been approved for release  
to the public by:

*7 Mercury*  
**2705**  
*David E. Hammin* 4/29/96  
Technical Information Officer Date  
ORNL Site

TO: A. M. Weinberg  
FROM: AD-HOC Committee on Mercury  
SUBJECT: ORNL - Y-12 and the Hg Problem in Tennessee

Concern about Hg in the nation's streams and lakes is approaching an almost hysterical level and Tennessee is one of the states most affected. It seems to us that the Laboratory can make an immediate and significant contribution to the solution of some aspects of the mercury pollution problem, at least in Tennessee and/or the TVA region and probably for the nation as a whole. This service could be a highly visible, positive demonstration of our ability to react quickly and effectively to environmental crisis-like situations. Probably we should make our capabilities more explicitly known to Walter Lambert, Chairman of the Governor's Committee on Mercury. Jack Gibbons has been in touch with Lambert concerning possible Hg contamination of White Oak Creek and Melton Hill reservoir which N. E. Bolton has been monitoring, and Jack has alluded to additional ORNL expertise and interest.

ORNL and Y-12 have already become involved with the Hg problem to some extent since Heinrich Malling of the ORNL Environmental Mutagen Information Center was appointed by Senator Gore to a committee to study the situation in Tennessee and to make recommendations to President Nixon and Tennessee Congressmen. Also, a meeting was held in John Googin's office between ORNL and Y-12 staff members and a representative from the Olin Corporation, Theodore Heying, Technical Director of the Division of Chemical Research. As a result of the meeting, assistance was offered and subsequently specimens from Olin's Charleston, Tennessee, Chlorine-caustic Soda Plant were sent to Bill Lyon for analysis. This meeting was the result of a call for help from Dr. W. E. Hanford of Olin to Glen T. Seaborg.

As you know, some of the NSF Project activity is focused on the resource and environmental concerns for Hg. During these studies, some of us had begun to realize that there is a wealth of Hg expertise and experience at both the Laboratory and at Y-12. Last Friday we convened a meeting at which the following important capabilities were identified:

1. The neutron activation analysis technique for Hg developed by Bill Lyon and his colleagues is unique in Tennessee. It is especially important since it measures true total Hg content in samples in any physical state (water, bottom sediments, effluents, fish, etc.) and

often it is possible to make the analysis without even removing the sample from its container. This method can detect amounts as small as  $10^{-9}$  gm of Hg and true totals result, in the sense that problems like volatility, adsorption, and complexation which may confound other methods (for example, the "accepted" atomic adsorption method) are not serious. Although this technique is relatively expensive, it should be used to check the validity of other methods, e.g., an improved X-ray fluorescence method proposed by Cullie Sparks which might offer a relatively cheap, dependable total Hg analysis and that also holds promise for on-line process monitoring.

The zonal centrifuge is being used by Paul Bonner to separate fractions of river-bottom sediments and water-suspended solids in a study of various forms of phosphorous in the environment. The technique should be applicable to support the chemical-analytical methods for Hg.

2. Over the years considerable experience with the separation of Hg from waste streams has been accumulated at both ORNL and Y-12 which could be of immediate usefulness to companies like Olin. Walt Clark has experimented successfully with the removal of Hg from acid waste streams using packed beds of Cu and also using FeS. Tom Handley extracted down to a few ppb of Hg from aqueous solutions using organic phosphorous-sulfur solvents prepared by W. H. Baldwin. It may be possible to synthesize a polymer with the same active groups which could be used as an ion exchanger for Hg in conventional exchange equipment. At Y-12, John Googin has used lithium amalgams as well as co-precipitation with CdS to remove Hg from effluents effectively and on a large scale. However, the state is requiring Olin to clean its waste streams down to a concentration of 5 ppb (the standard for drinking water) and to do this effectively and economically may take considerable research.\*

3. We have a unique capability for studying the ecological effects of Hg. Dan Nelson and Gerry Ulrikson have already initiated an experiment to discover the biological half-life of Hg in fish. The experiment should also show what percentage of Hg comes directly from the water and what percentage through food. Results should be forthcoming in a few months. These data will be useful in relating water quality standards for Hg to potential hazards associated with human consumption of fish from Hg contaminated environments.

4. Of long range significance are the studies of Heinrich Malling and Fred de Serres on the genetic effects of Hg.

In view of these considerable capabilities, we wonder if it might not be possible to ask the AEC to sponsor for the next several months a special task force from ORNL - Y-12 to help the state with the Hg crisis. This task force could work with the state and TVA to determine the scope of the problem by identifying the sources and flow patterns of Hg, to provide consultation and technical assistance to industries concerning removal of Hg from waste streams, and to establish a better

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\*In this regard the experience and ideas of the Water Research Program should be very important.



August 10, 1970

basis for setting standards for Hg control.

A four-man task force for six months should be sufficient, considering the related activities of the NSF Project with regard to Hg. These activities include studies of the basis for and difficulties with the establishment of Hg standards and of the problems with increasing Hg recycle. In addition, the project has begun to assemble and organize the available information on this element which will be necessary to determine the full scope of the problem and indicate necessary research.

We would very much like to discuss our suggestion for action with you as soon as possible.

*Bill Fulkerson*

W. Fulkerson  
NSF Summer Study

WF:jab

Committee on Hg:

W. H. Baldwin  
W. P. Bonner  
N. E. Boulton  
Richard Brown  
W. E. Clark  
K. E. Cowser  
F. J. de Serres  
W. Fulkerson  
J. H. Gibbons  
V. E. Giuliano  
J. M. Googin  
T. H. Handley  
R. W. Knight  
W. J. Lyon, Jr.  
H. V. Malling  
W. R. Martin  
Daniel Nelson  
S. A. Reed  
W. D. Shults  
C. J. Sparks, Jr.  
G. Ulrikson  
R. A. Wallace  
J. S. Wasson

cc: F. L. Culler  
J. L. Liverman  
D. J. Rose  
D. B. Trauger  
Committee on Hg

*Agan Lucas*

## Strontium-90, Strontium-89, Plutonium-239, and Plutonium-238 Concentrations in Ground-Level Air, 1964-1969

Bernard Shleien, Joseph A. Cochran, and Paul J. Magno

Northeastern Radiological Health Laboratory, Bureau of Radiological Health, Environmental Health Service, Winchester, Massachusetts 01890

■ Data are presented on monthly concentrations of strontium-90, strontium-89, plutonium-239, and plutonium-238 in ground-level airborne particulates collected in Winchester, Mass., from October 1963 (for radionuclides of strontium) and May 1965 (for radionuclides of plutonium) to March 1969. The ratio of the activities of strontium-89 to strontium-90 in these samples indicates an influx of strontium-90 following all but the sixth Chinese atmospheric detonation. In 1968, approximately 60% of the strontium-90 present in ground-level air was of post-1963 origin. The ratio of the activities of plutonium-239 to strontium-90 prior to February 1968 was  $0.017 \pm 0.009$ . There was a gradual increase in the above ratio later in 1968 which is attributed to debris from the sixth, seventh, and eighth Chinese tests. Levels of plutonium-238 in SNAP-9A debris in ground-level air during 1968 were 80% to 50% lower than had been predicted.

The radionuclides strontium-90, strontium-89, plutonium-239, and plutonium-238 are present in the atmosphere as the result of nuclear weapons tests. In the case of plutonium-238, in addition to the above source, Harley (1964) reported that an injection of this radionuclide into the atmosphere took place in April 1964 when 17 kilocuries of plutonium-238, contained in a SNAP-9A power source, burned up south of the equator off the coast of Africa. Information on airborne strontium and plutonium isotopes is of interest in evaluating the potential health hazards of these materials and in investigating the transport processes involved. Analysis of ground-level airborne particulate samples for the radionuclides of strontium has been performed at the Northeastern Radiological Health Laboratory (NERHL) since October 1963. For the plutonium isotopes, radiochemical and alpha spectroscopic analysis has been performed since May 1965. These isotopes include plutonium-239, plutonium-240, and plutonium-238. The energies of the alpha particles from plutonium-239 and plutonium-240 are not sufficiently different to be separated by alpha spectroscopy. Therefore, when plutonium-239 is referred to, it is meant to represent the sum of the activities of plutonium-239 and plutonium-240.

Results of these analyses to April 1966 (for strontium-90) and to February 1967 (for the plutonium isotopes) have been previously reported (Magno, *et al.*, 1967; Shleien and Magno, 1967). Extensive measurements of these radionuclides in air particulates and precipitation have been performed by the Health and Safety Laboratory (HASL) of the Atomic Energy Commission for several years (Volchok, 1969). In addition, the Joint Nuclear Research Center, ISPRA Establishment,

Italy, has published data on SNAP-9A plutonium-238 (DeBortoli and Gaglione, 1969).

This paper presents results on ground-level airborne concentrations of the above radionuclides from the inception of the sampling and analysis program at NERHL to March 1969. Shleien (1969), in recent assessment of doses from these radionuclides based on the concentrations presented in this paper, indicates that only an infinitesimal portion of the total strontium-90 dose to bone is due to inhalation of airborne material. On the other hand, the dose from plutonium-239 to the tracheobronchial lymph nodes was reported to be 160 millirem in 50 years, second in magnitude only to the dose from strontium-90 (from ingestion) to the bone. According to the same investigator, the dose from plutonium-238 to this lymphatic tissue was about one-quarter of that from plutonium-239. In this publication, attention will be given to the origin of these radionuclides and to the contribution of various atmospheric nuclear tests and the burnup of the SNAP-9A satellite to the total quantity of the radionuclides present in ground-level air. A summary of reported atmospheric detonations which occurred during the period of this study is given in Table I.

### Methodology

Monthly composite particulate samples, representing 12,000 m.<sup>3</sup> of air, are collected on 8 × 10-inch membrane filters (pore size, 0.8 micron) at a height of 1 m. above the ground. The samples are wet ashed with a mixture of nitric and perchloric acids. The sample is split into two parts for radiochemical analysis.

One-half the sample is analyzed for strontium-90 and strontium-89 as follows (U.S. Dept. HEW, 1967): Strontium carrier is added and the strontium is precipitated from the samples first as the carbonate then as the nitrate. Further purification is made by barium chromate precipitation and hydroxide scavenging. After an ingrowth period, yttrium carrier is added and the yttrium is extracted into TTA (2-thenolytrifluoroacetate) at pH 5.0. The yttrium is stripped from the TTA with dilute nitric acid, precipitated as the oxalate and beta counted for yttrium-90. The strontium is precipitated as the carbonate and beta counted for total radiostrontium. The strontium-89 activity is calculated from the total radiostrontium measurement after correction for the strontium-90 content.

Analysis of the other half of the sample for the plutonium isotopes is briefly described below (U.S. Dept. HEW, 1967): Plutonium-236 tracer is added, the plutonium reduced to the +3 state and coprecipitated with lanthanum fluoride. The lanthanum fluoride is converted to lanthanum hydroxide, dissolved in 7.2 M nitric acid and the plutonium oxidized to the +4 state. The solution is passed over an anion

exchange resin in the nitrate form. The resin is washed with additional nitric acid and then with 9 M hydrochloric acid. The plutonium is then eluted from the resin with a mixture of 0.36 M hydrochloric acid and 0.01 M hydrofluoric acid, electroplated onto a stainless steel planchet from a sulfuric acid-ammonium sulfate electrolyte. The 5.15 MeV alpha particle of plutonium-239 and the 5.48 MeV alpha particle of plutonium-238 are counted with a silicon surface barrier detector linked to a multichannel analyzer. With the sample electroplated onto a 3.1 cm.<sup>2</sup> area, the counting efficiency is ~31% and the resolution 75 KeV (width at half-peak height).

The minimum detectable concentrations are 0.10, 0.40, and 0.003 fCi/m.<sup>3</sup> for strontium-90, strontium-89, and the plutonium isotopes, respectively. The strontium-90 represented by the 2 $\sigma$  counting error did not exceed 25% of the corresponding sample value and was approximately 10% in the majority of cases. The corresponding values for strontium-89 are about twice as high. The maximum 2 $\sigma$  counting errors are 50% and 67% of the reported values for plutonium-239 and plutonium-238, respectively, but are appreciably lower as the results increase above the minimum detectable levels.

### Results and Discussions

The results of strontium-90 analyses of ground-level airborne particulates from monthly composite samples are presented in Figure 1. Difficulties in sampling and analysis caused the loss of two samples (October 1963 and August 1967), and during a change-over in personnel responsible for collection and analysis of the data, several months of ambiguous data (September, October, November, and December 1967) occurred. Figure 1 illustrates the expected spring maximum which occurs each year and which appears to be extremely reproducible in terms of time of appearance. A line (solid) indicating the expected spring maximum highs, based on the

Table I. Reported Atmospheric Detonations

Date	Source	Comments
October 16, 1964	Chinese (1st)	Low <sup>a</sup>
May 14, 1965	Chinese (2nd)	Low
May 9, 1966	Chinese (3rd)	Intermediate <sup>b</sup>
July 2, 1966	French	70-80 KT
July 19, 1966	French	120 KT
September 24, 1966	French	150 KT
October 4, 1966	French	Intermediate <sup>b</sup>
October 27, 1966	Chinese (4th)	Low-intermediate <sup>c</sup>
December 28, 1966	Chinese (5th)	Few hundred KT
June 5, 1967	French	Low
June 17, 1967	Chinese (6th)	2 MT
June 27, 1967	French	Low
July 3, 1967	French	Low
December 24, 1967	Chinese (7th)	MT range
July 7, 1968	French	Low
July 15, 1968	French	Low
August 3, 1968	French	Low
August 24, 1968	French	2 MT
September 9, 1968	French	2 MT
December 28, 1968	Chinese (8th)	2 MT

<sup>a</sup> Less than 20 KT.

<sup>b</sup> 200-300 KT.

<sup>c</sup> 20-200 KT.

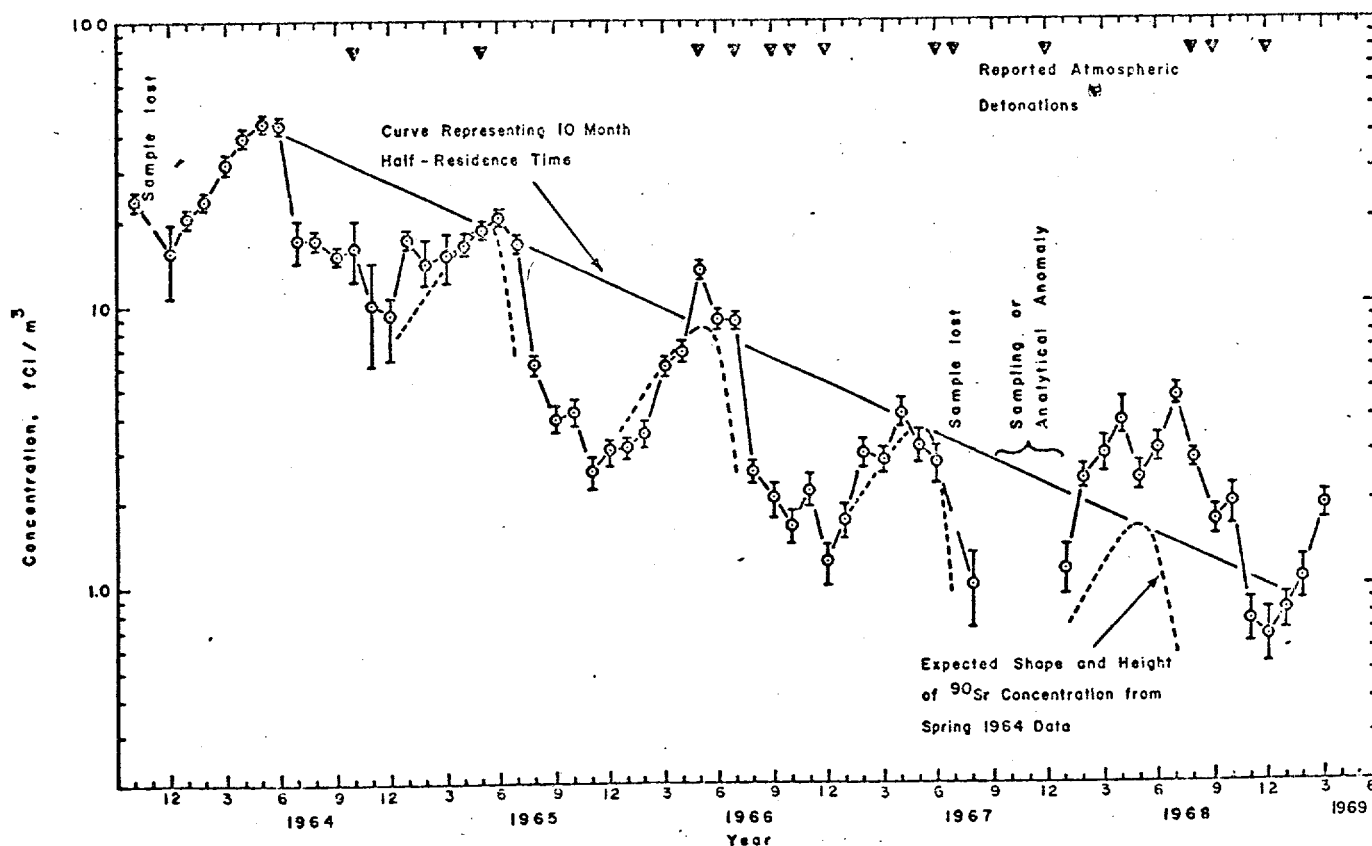


Figure 1. Strontium-90 in ground-level air

strontium-90 concentrations in the spring of 1964 and a stratospheric residence half-time of 10 months (Telegadas, 1969), is shown. The expected strontium-90 curve (dashed), having the shape of the 1964 curve because no fresh intrusion of material occurred until the end of that year, is also shown. The difference in the expected and actual curves indicates strontium-90 of post-1963 origin was present.

A double peak in strontium-90 levels appears in 1968. Although not apparent from this study, Thomas (1969) has noted the presence of fresh fission products during August 1968 and attributes the rise in radioactivity to the rapid movement of debris from the French tests in July 1968. Strontium-90 levels in the latter part of 1968 would be elevated if such an intrusion occurred. Another possibility is an influx of strontium-90 of stratospheric origin, although this is not apparent from the strontium-89 to strontium-90 ratios discussed later.

Strontium-89 concentrations are shown in Table II. Strontium-89 values are indicated only in months where the levels of this radionuclide were above the minimum detectable level. All the appearances of strontium-89 followed Chinese atmospheric tests. This fact, together with the information that, except in the case noted above, the French tests were not

measurable at 10° N latitude (Hardy, 1968), appears to make the Chinese detonations the principal source of increases above the expected strontium-90 levels.

The contribution of strontium-90 from a particular test may be estimated from the strontium-89 to strontium-90 ratio. These estimates are also presented in Table II. The theoretical ratios are based on production yield of strontium-90 and strontium-89 from uranium-235 fission (Weaver, *et al.*, 1963) and are corrected for decay time between the nuclear test and the time of collection. In most cases, the contribution of strontium-90 in ground-level air from a recent nuclear test, based on the strontium-89 ratios, appears to be of tropospheric origin. However, the strontium-89 to strontium-90 ratio following the fifth Chinese test appears to be influenced by the presence of strontium-89 of stratospheric origin beginning in March of 1967, as evidenced by the initial decrease and subsequent increase in the strontium-89 to strontium-90 ratio.

Early low yield tests contributed only small amounts to ground-level strontium-90 concentrations. The fifth Chinese test (December 27, 1966) appears to have contributed a substantial quantity of strontium-90. There was no evidence of a fresh strontium-90 intrusion following the sixth Chinese test (June 17, 1967), although complete data are not available.

Table II. Strontium-89 Concentrations and Contribution of Fresh Strontium-90 from Atmospheric Tests

Test and date	Sample collected (month and year)	<sup>89</sup> Sr concentration (fCi/m. <sup>3</sup> )	Time elapsed since test (days)	Ratio <sup>89</sup> Sr to <sup>90</sup> Sr		<sup>90</sup> Sr from test (%)
				Theoretical	Measured	
Chinese, #1 (Oct. 16, 1964)	Nov. 1964	10 ± 3 <sup>a</sup>	30	111	1.6	1.5
	Dec.	ND <sup>b</sup>	60	74	ND <sup>b</sup>	...
	Jan. 1965	16 ± 3	91	49	0.8	1.6
Chinese, #2 (May 14, 1965)	June 1965	57.9 ± 2.7	30	111	2.9	2.6
	July	28.2 ± 2.6	60	74	1.7	2.3
	Aug.	2.4 ± 1.1	90	39	0.3	0.8
	Sept.	1.5 ± 1.2	120	33	0.4	1.2
Chinese, #3 (May 9, 1966)	June 1966	13.1 ± 2.8	37	100	1.8	1.8
	July	10.4 ± 1.7	67	67	2.2	3.3
	Aug.	4.3 ± 0.8	108	38	1.7	4.5
	Sept.	1.8 ± 0.7	139	25	0.9	3.6
Chinese, #4 (Oct. 27, 1966)	Nov. 1966	18.7 ± 1.7	19	129	8.5	6.6
	Dec.	6.5 ± 0.8	49	86	5.3	6.2
Chinese, #5 (Dec. 27, 1966)	Jan. 1967	11.9 ± 1.2	19	129	7.0	5.4
	Feb.	15.5 ± 1.1	49	86	5.3	6.2
	March	27.4 ± 1.6	81	55	9.9	18
	April	34.7 ± 1.6	112	36	8.5	23
	May	14.0 ± 1.8	142	24	4.5	19
	June	5.3 ± 0.9	173	16	2.0	13
Chinese, #6 (June 17, 1967)	No evidence of <sup>89</sup> Sr in Aug. or Sept. 1967.					
	July sample lost and Sept. through Dec. sampling or analytical ambiguities occurred					
Chinese, #7 (Dec. 24, 1967)	Jan. 1968	6.5 ± 0.6	22	124	5.8	4.7
	Feb.	18.3 ± 1.1	53	81	7.2	11
	March	14.8 ± 1.1	81	55	5.1	9.3
	April	13.1 ± 1.1	111	36	3.4	9.5
	May	3.1 ± 0.7	141	24	1.3	5.5
	June	2.9 ± 0.7	172	16	0.9	5.6
Chinese, #8 (Dec. 28, 1968)	Feb. 1969	2.3 ± 0.5	48	87	2.2	2.5

<sup>a</sup> 2σ counting error.

<sup>b</sup> ND: Not determined.

For the two months following this test, for which results were available, there was no indication of elevated strontium-89 levels. Data from HASL also indicate the absence of strontium-89 from this test (Hardy, 1968). Peirson and Sisefsky (1969) have suggested that this device exploded at a comparatively low altitude (14 km.), but that the bulk of the debris was carried to a high altitude by the rising fireball.

From the differences in projected and actual levels of strontium-90, an estimate of the strontium-90 from atmospheric testing after 1963 can be made. Table III presents the mean predicted (based on a 10-month residence half-time and the mean 1964 results) and measured strontium-90 concentrations in ground-level air. Because of the magnitude of errors in analyses, only the values for 1968 are truly significant, although there are indications of newly injected strontium-90 since 1965. In 1968, 62% of the total ground-level strontium-90 was due to post-1963 tests. Volchok (1969) estimates that 71% of the total reservoir of strontium-90 in 1968 could be attributed to post-1963 debris.

Concentrations of plutonium-239 in ground-level air particulates are presented in Figure 2. The pattern of minimums and maximums is similar to that for strontium-90. The same limitations (sample loss and ambiguity) hold as for the strontium-90 data. The average ratio of the activities of plutonium-239 to strontium-90 for the period May 1965 through February 1968 was 0.017 with a  $2\sigma$  range of  $\pm 0.009$ . There is a gradual rise in this ratio following this period, the average value being 0.028 from March 1968 to March 1969. This increase in the plutonium-239 to strontium-90 ratio is attributed to the sixth, seventh, and eighth Chinese tests, which were reported to be high yield events.

The ratio of plutonium-238 to plutonium-239 remained relatively constant at  $0.04 \pm 0.02$  from May 1965 to July 1966. A change in the ratio was fairly evident at NERHL in mid-

Table III. Estimated Contribution of Post-1963 Tests to  $^{90}\text{Sr}$

Year	Mean $^{90}\text{Sr}$ (fCi/m $^3$ )		Estimated contribution post-1963 tests (%)
	Predicted	Measured	
1964	24.1 <sup>a</sup>	24.1	...
1965	10.5	11.3	7
1966	4.6	4.6	...
1967	2.0	2.3 <sup>b</sup>	15
1968	0.9	2.4	62

<sup>a</sup> Predicted value based on measured results for 1964.

<sup>b</sup> No data for July, October, November, and December.

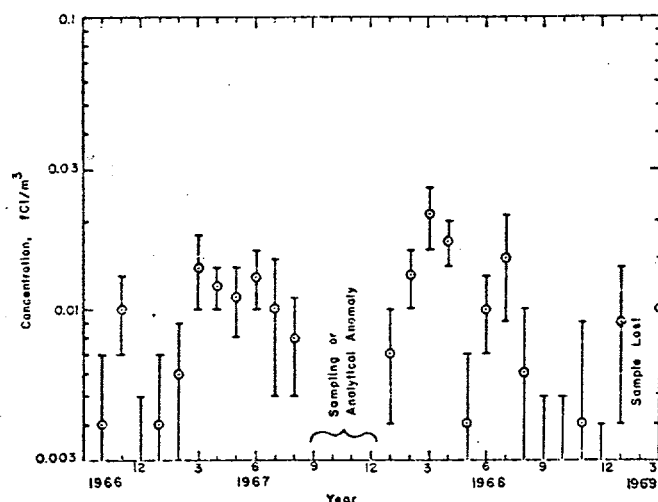


Figure 3. Estimated SNAP-9A plutonium-238 in ground-level air

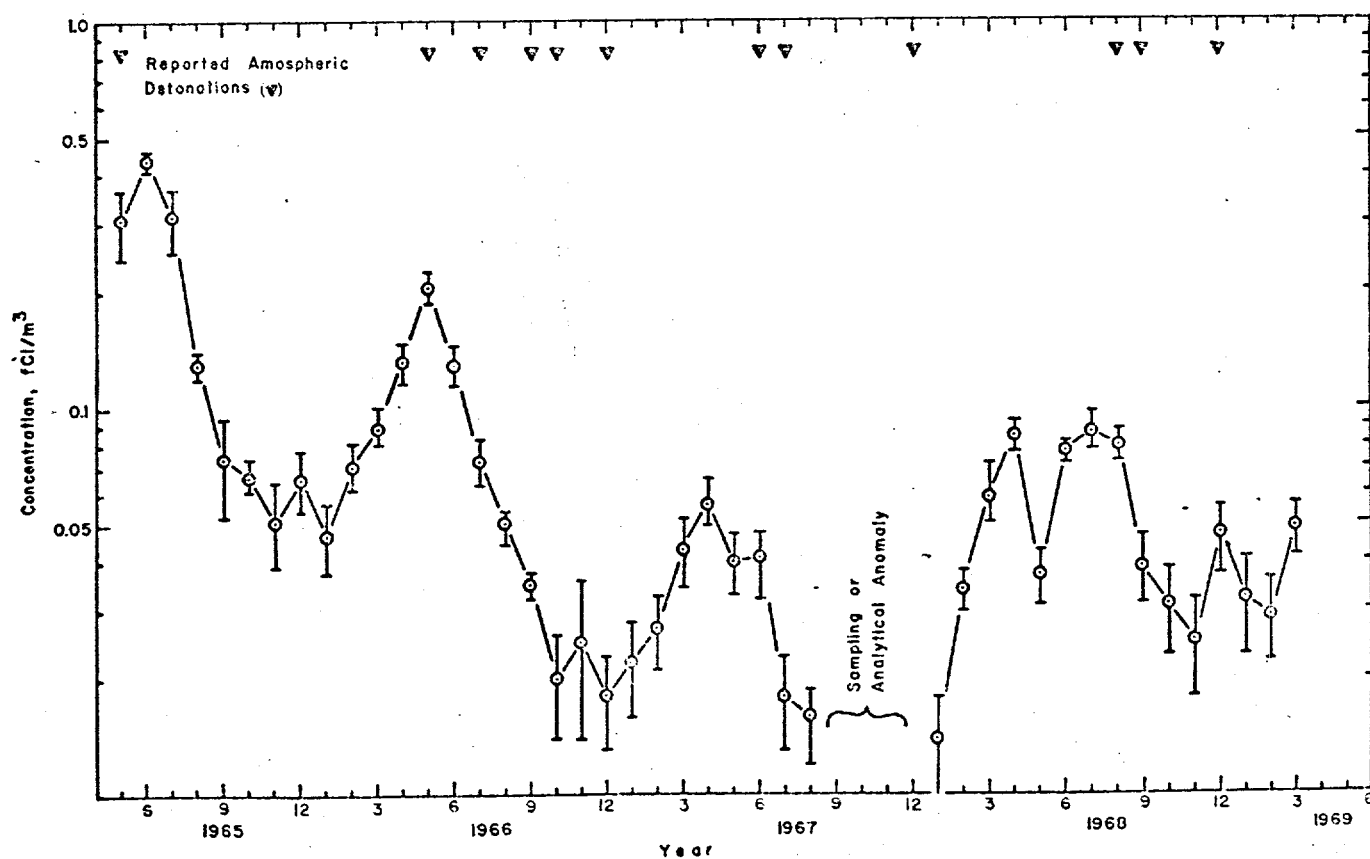


Figure 2. Plutonium-239 in ground-level air

Table IV. SNAP-9A Plutonium in Ground-Level Air (fCi/m.<sup>3</sup>)

Date	Predicted	ISPR	NERHL
Jan. 1966	0.011	0.001	...
July 1966	0.013	0.003	...
Jan. 1967	0.015	0.005	0.004
July 1967	0.016	0.015	0.011
Jan. 1968	0.017	0.012	0.014
July 1968	0.018	...	0.010

1966 (Shleien and Magno, 1967). This change in ratio indicated a new source of plutonium-238 other than that which was previously present. DeBortoli and Gaglione (1969) announced this change in plutonium-238 to plutonium-239 ratio somewhat earlier in June and July of 1966, the conclusion being that SNAP-9A plutonium-238 had reached ground level in the northern hemisphere.

Figure 3 is a plot of the SNAP-9A plutonium-238 concentrations in ground-level air based on the above ratio of plutonium isotopes prior to influx of the satellite debris. The levels of SNAP-9A plutonium-238 are slightly elevated over the 1967 levels. This elevation is expected, based on prior predictions (Volchok, 1966) of increasing plutonium-238 levels in 1968. These predictions anticipated that plutonium-238 from SNAP-9A would behave similarly to rhodium-102 and cadmium-109 which were used as tracers in high altitude nuclear tests in 1958 and 1962. A comparison of the predicted results, the reported results at ISPR, and NERHL results is presented in Table IV. In 1968, the NERHL results (3-month averages) are 80% to 50% lower than the predictions.

## COMMUNICATION

### Automated Method for Determining and Removing Silica Interference in Determination of Soluble Phosphorus in Lake and Stream Waters

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Values obtained for soluble P in the low  $\mu\text{g./l.}$  range in lake and stream waters were found in some cases to be higher than total P values. This error is shown to be due to silica that gives an apparent P reaction with ammonium molybdate. This error is of importance when P is to be determined in the low  $\mu\text{g./l.}$  range. A method is presented to permit an automated simultaneous determination of soluble P and the silica interference so that a correction can be made.

In a recent project to define partially the water quality, weed growth, and nutrient content of streams flowing into Canal Lake, Ontario, it was necessary to establish Auto-Analyzer techniques to operate in the  $\mu\text{g./l.}$  range for soluble and total phosphorus. Perhaps the principle nutrient involved in the eutrophication process (Campbell and Webber, 1969).

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Soluble P, the fraction that reacts with ammonium molybdate without hydrolysis, is the most frequently determined parameter in water analysis. In developing these techniques, we became aware of a silica interference that appeared to give false soluble P values by the methods used. This interference was illustrated by lower total P than soluble P. Silica is dehydrated during the  $\text{HClO}_4$  digestion for total P and thus does not interfere with the total P determination. Silica has always been considered a potential interference in P determinations involving the phospho-molybdate complex, but in most cases P is determined in the  $\text{mg./l.}$  range where Si does not give significant interference except at concentrations over about 100  $\text{mg./l.}$  of  $\text{SiO}_2$  (Standard Methods, 1965).

The amount of silica in groundwater is controlled by the minerals in contact with the water and should range from about 6  $\text{mg./l.}$  in equilibrium with quartz to about 140  $\text{mg./l.}$  in equilibrium with amorphous silica (Polzer, 1967). For example, values of 1 to 45  $\text{mg./l.}$  of silica have been reported in